Inducing Polymer Interphase Formation in the Composite at Low Nano-Carbon Loading

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ABSTRACT

The addition of the nano-carbon fillers is expected to improve the corresponding mechanical properties of the polymer matrix for high-performance fiber productions. This increase in the properties depends on the distribution of nano-carbons, as well as the interaction between the polymer and the filler. This work focuses on understanding how the nano-carbons can affect the formation of the polymer interfacial morphology to form self-reinforcement polymer-interphase regions in the composite. This study outlines the analysis of composites with low nano-carbon loadings (<1 wt%) in order to study this structure-property relationship. The results have shown that predominant interphase growth led to the significant mechanical property increase, corresponding to highest polymer chain orientation, longest lamellar height, and most compact crystal packing structures.

Keywords: nanocomposite fibers, polymers, interphase, mechanical properties, X-ray

1 INTRODUCTION

Fabrication and post-treatment of high-performance nano-composite fibers are gaining more significance because of their unique anisotropic mechanical properties and wide applicability to areas in the automotive, aerospace and medical industries. In order to fully take advantage of the potential of these materials in terms of their predicted mechanical and thermal properties, fundamental issues to be addressed include, (i) nano-filler dispersions, (ii) polymer-filler nano-scale interactions at the interfacial regions, and (iii) orientation of the filler and matrix molecules [1]. Most current studies (to control the aforementioned properties of polymer-based nano-composite fibers) have focused on tailoring the fiber spinning methods or changing the nano-fillers. However, studies related to the effects of low filler concentration in conjunction with the morphology-microstructure-performance relationship of fibers have been so far limited.

Previous work also has shown that modification polymer matrix morphology due to the presence of the nano-filler particles can further improve the mechanical properties (i.e., lubrication [2] and crystallization nucleation and templating effects [3, 4]). Accordingly, polymer/nano-carbon fibers exhibit drastic differences in crystallinity and chain conformations (i.e., extended-chain crystals) depending on the filler loading and dispersion. In this paper carbon nano-chips (CNC) was introduced into semicrystalline polymer, poly(vinyl alcohol) (PVA) to spin composite fibers at low loadings. Studies of how the presence of this nano-carbon can promote interphase polymeric growth and also influence the composites microstructure was conducted. Tensile testing, dynamic mechanical analysis (DMA), wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were used to characterize the properties for both control PVA and composite fibers.

2 MATERIAL AND METHODS

2.1 Materials

As-produced, nano-chips (i.e., flattened FWNT with equal length and width ~ 100 nm, and purity > 99 wt%) stack to form fibers. CNC were purchased from Catalytic Materials LLC (the stacked fibers have width 100 nm and average length 1000 nm, up to 10,000 nm in maximum, density ~2.2 g·cm⁻³, and surface area ~120 m²·g⁻¹). Movial 56-98 PVA (M_w ~105,600 g·mol⁻¹, degree of hydrolysis 98.4 ± 0.4 mol%, residual acetyl content 1.5 ± 0.4 wt%) was obtained from Kuraray America. Dimethyl sulfoxide and methanol were purchased from Fisher Scientific.

2.2 Spinning Method

The PVA solution was made by dissolving 2.4 g PVA solid particles in 30 ml DMSO at ~100 °C. For the composite solutions, PVA was first dissolved into DMSO, while 0.6 g CNC was sonicated in 40 ml DMSO for 2 hrs. For better dispersions, the former PVA solution was added into the sonications (Fisher F530 bath sonicator, 43 kHz, 150 W) for another 24 hrs. To remove larger agglomerations, the dispersed mixtures were centrifuged with rate of 14 kRPM for 60 min. Subsequently, the remaining PVA and DMSO were mixed together with the CNC dispersion taken from the top level of vials. The
subsequent concentrations of CNC were 0.125, 0.25, 0.5, and 1 wt% in the composite solutions.

A shear-flow assisted gel-spinning apparatus [5], was used to spin both the control and the composite fibers. A syringe pump is used to inject the spinning dope through a needle (22-gauge) into the glass tube, at a rate of ~0.5 ml·min⁻¹. Methanol is pumped through the glass tube at a rate of 0.4 ml·min⁻¹. This shear flow provides drawing to the as-spun fiber, while the methanol acts as the coagulant. The fibers were then collected on take-up rollers (rate ~20 to 25 m·min⁻¹).

2.3 Post-spinning Treatment

As-spun fibers were post-processed by heat-drawing procedures. The drawing procedure was conducted on rectangular hot plate (10 inches by 1 inch) for three heating stages of 100, 160, and 200 °C, respectively. Considering the moisture absorption of PVA itself, all fibers were stored in a desiccator before testing and characterization.

2.4 Characterizations

Tensile tests were conducted using dynamic mechanical analyzer (RSA-G2 series, manufactured by TA Instruments) with the gauge length of 20 cm and extension rate of 0.05 mm·min⁻¹. The number of samples tested ranged from 10 to 15. The RSA-G2 was also used for dynamic mechanical tests in tension mode within the temperature of −80 to 250 °C at a step-size of 3 °C·min⁻¹. Frequency was fixed to 1 Hz, the maximum tension was set to be 0.2% (0.04 mm displacement for 20 mm gauge length), and the tension controlled to ensure that the static force always exceeded the dynamic force by 20%. With good reproducibility, 3 to 5 bundle samples consisting of 30 filaments in each bundle were measured. Wide-angle X-ray diffraction was performed on a Rigaku RAPID II curved detector X-ray diffraction system equipped with a 3 kW sealed tube source. XRD curve fitting and analysis was performed using software’s PDXL2 and 2DP to obtain azimuthal integration data as well as peak widths (i.e., full-width at half maximum [FWHM]). Small-angle X-ray scattering were performed using a Micro-MAX 3000 +007 HFM SAXS system with CuKα radiation, equipped with a 200 nm multiwire two-dimensional detector, manufactured by Rigaku Americas. Small-angle scattering patterns were analyzed using SAXS GUI.

3 RESULTS

3.1 Tensile Tests

The static mechanical properties for both PVA and PVA/CNC fibers were measured. Stress-strain curves are plotted in Figure 1 and properties listed in Table 1. An increasing trend is observed for both the modulus and tensile strength from the control to 0.5 wt% composite fibers. At 1 wt% loading, it was observed that the CNC dispersion is reduced as the content becomes higher (i.e., agglomerations form), therefore lower modulus and strength values are measured.

![Figure 1: Stress-strain curves for all fibers drawn at 200 °C.](image)

<table>
<thead>
<tr>
<th>loading</th>
<th>0</th>
<th>0.125</th>
<th>0.25</th>
<th>0.5</th>
<th>1</th>
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<tbody>
<tr>
<td>E</td>
<td>27.20 ± 3.48</td>
<td>39.51 ± 8.32</td>
<td>47.61 ± 7.57</td>
<td>60.45 ± 5.95</td>
<td>57.96 ± 4.91</td>
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<tr>
<td>σ</td>
<td>1.18 ± 0.35</td>
<td>1.52 ± 0.24</td>
<td>1.42 ± 0.18</td>
<td>2.20 ± 0.27</td>
<td>1.61 ± 0.12</td>
</tr>
<tr>
<td>ε</td>
<td>6.88 ± 2.33</td>
<td>5.24 ± 0.80</td>
<td>5.45 ± 1.20</td>
<td>7.46 ± 3.97</td>
<td>4.31 ± 0.20</td>
</tr>
<tr>
<td>T</td>
<td>40.11 ± 6.10</td>
<td>31.40 ± 8.51</td>
<td>32.64 ± 5.91</td>
<td>73.43 ± 21.28</td>
<td>27.17 ± 2.36</td>
</tr>
</tbody>
</table>

Table 1: Modulus (E), strength (σ), strain (ε) and toughness (T) of all tested final stage fibers.

In addition to the modulus and strength, Table 1 also shows the very high toughness values for 0.5 wt% composite fibers, due to high tensile strength and relatively large tensile strain as compared to many high-performance fibers (i.e., Kevlar®, Spectra®, and carbon fibers).

3.2 Dynamic Mechanical Analysis

Dynamic properties of the fibers were measured using a DMA, and storage modulus E′, loss modulus E″ and tan δ are plotted against temperature (Figure 2). The trend of E′ and E″ varied similarly to the static tensile property data, as shown in Figure 2a and b.

Based on the tan δ data for the control and the composites (Figure 2c), four transitions are identified. The lower transition (~25 to 0 °C) is related to the rotation of functional groups or local back-bone/main-chain movement, and is referred to as the β transition. The higher transition (40 to 60 °C, α1) and even higher transition temperature (80 to 100 °C, α2) are related to the glass transition of the PVA. Both β and α1 transitions have an increase of around 10 to 15 °C from the control to the composite fibers. The α2 transition is significantly increased in the composites as compared to the control fibers (up to ~36 °C in 0.5% loading), as shown in Figure 2c. Since glass transition involves cooperative segmental motion, the presence of the CNC fillers reduces polymer chain mobility.
by restricting both side-group rotations and global backbone motions.

The suppression of $\tan \delta$ became more pronounced from control PVA to composite fibers. This also suggests more restricted polymer chain movement considering that $\tan \delta$ is defined as storage modulus and loss modulus ratio, and higher ratio implies the presence of stiffer regions and more crystallized polymer chains.

Figure 2: DMA curves for all fibers at 200 °C drawn stages, (a) storage modulus ($E'$), (b) loss modulus ($E''$) and (c) the tangent of mechanical loss angle $\delta$ ($\tan \delta$).

### 3.3 Wide-angle X-ray Diffraction (WAXD)

The WAXD patterns of the fibers at various loadings are shown in Figure 3. WAXD data can be used to determine the degree of orientation ($f_c$), is given by the Herman’s equation (1) and (2) [6]:

$$f_c = \sqrt{\frac{3<\cos^2 \phi_c>-1}{2}}$$

$$<\cos^2 \phi_c> = \frac{\int_0^{\pi/2} \cos^2 \phi_c \sin \phi_c I(\phi_c) d\phi_c}{\int_0^{\pi/2} I(\phi_c) \sin \phi_c d\phi_c}$$

$\phi_c$ is the azimuthal angle, and $\phi_c = 0$ corresponds to the fiber axis direction. The value of $<\cos^2 \phi_c>$, the average value $\cos^2 \phi_c$, is determined from the azimuthal distribution of intensity $I(\phi)$, assuming cylindrical symmetry about the fiber axis.

Figure 3: Wide-angle X-ray showing that the polymer chain orientation is significantly enhanced along fiber axis with nano-carbon inclusion. 0.5 wt% fibers drawn at 200 °C exhibit highest orientation for PVA for these fiber samples.

The calculated orientation factor increase from 0.6 for control PVA fibers to as high as 0.8 for the 0.5 wt% composites. Better oriented polymer chains would contribute to the modulus increase observed. The degree of crystallinity ($\chi_c$) was also determined by WAXD and is calculated using equation (3) where $I_c$ and $I_a$ are taken from the intensity $I(\theta)$ vs. scattering angle plots [7]:

$$\chi_c = \frac{I_c}{I_c + I_a} \times 100\%$$

$I_c$ and $I_a$ are the total intensity scattered by the crystalline and amorphous regions, respectively. Processing results showed similar $\chi_c$ among fibers lower than 0.5 wt%, within a range of 50 to 54%. 1 wt% composites instead showed higher $\chi_c$ value of 60%. This slight increase in crystallinity may be due to the presence of more CNC, which provided nucleation sites for crystal growth. In general through, crystallinity is comparable for all fibers produced here.

### 3.4 Small-angle X-ray Scattering (SAXS)

SAXS is commonly used to study the distribution of interlamellar and interfibrillar amorphous/crystalline regions in fibers by measuring the dimensions of equatorial diffuse scattering (EDS) and lamellar meridian peaks (LMP). Both the EDS and LMP are analyzed using the data provided by the equatorial streak and meridional lobes in Figure 4.

Figure 4: Small-angle X-ray scattering pattern showing that the lamellar spacing along fiber axis is significantly enhanced as the CNC loading increases.

Analysis of the patterns in Figure 4 showed that the lamellae length increased by around 2 to 3 nm while the lamellae diameter decreased for the composite. In addition,
the fibril increased by around 3 to 4 nm in length and width by 5 to 7 nm, from control to composite fibers.

4 DISCUSSIONS

It is generally believed that increase of crystallinity degree, crystal size, and better orientation of polymer chain will increase the mechanical properties. WAXD has shown the similar crystallinity degree between control and composites, however, the crystals present may be enough to account for the effective transfer of stresses in the material upon tension. The resultant fibers exhibit drastically enhanced properties when the CNC were evenly dispersed throughout the material. In these cases, the interphase region volume percent becomes larger (Figure 5) and increases the prevalence for effective interaction between the polymer matrix and nanofillers.

![Figure 5: Volume of crystallized and fully aligned interphase polymer fraction calculated from tensile properties, as a function of filler concentrations.](image)

A linear fitting of the mechanical modulus versus concentration of the filler (data shown in Table 1) was used to determine the effective modulus contribution in the composite. The effective modulus is the slope of the linear fit of the curve. $E$ is given in TPa and was found to be $2.8+6.8\chi$, where $\chi$ is the concentration weight fraction (i.e., 0, 0.00125, 0.0025, 0.005, and 0.01). A value of $\sim 6.8$ TPa for 200 °C drawn fibers was determined for the effective modulus. Similarly, the effective strength value is 188 GPa determined by the same analysis technique. Data reported by others showed effective modulus as high as 9.8 TPa and effective strength 0.3 TPa [8]. These values are much larger than the theoretically or experimentally measured intrinsic properties of nano-carbons [9, 10]. This analysis confirms the reasonable explanation that the polymer interphase growth provides additional self-reinforcement in tandem with filler reinforcement. For this reason, and interphase contribution and volume fraction percentage increase with filler content and is at the maximum at 0.5 wt% as shown in Figure 5. These interphase regions are responsible for providing self-reinforcement to the matrix (i.e., bulk polymer).

5 CONCLUSIONS

The precise description of interactions between filler and polymer is a key factor to study the nanocomposites reinforcement mechanism. Here, a facile and reproducible processing strategy allows us to obtain both the excellent properties and also multi-scale characterizations of fibers at various low-level loadings. Alternative analyses have shown that the interphase growth upon inclusion of nanofillers, in addition to the better orientated polymer chains. These regions act to self-reinforce the polymer composite beyond the filler leading to large the mechanical property increases beyond what is predicted by rule-of-mixture treatments.

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